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Volume 6

Polymer Reactions

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12

Synthesis of Graft Copolymers

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12.1 INTRODUCTION

Graft copolymers exhibit branched molecular structures. A supposedly linear main chain (the backbone) has attached to it polymeric side chains (the grafts) of different chemical nature, in most cases distributed randomly[1] (see Volume 3, Chapter 3). Interactions generally occur between backbone and grafts, resulting in a marked tendency to yield intramolecular phase separation in the bulk polymer (see Volume 2, Chapter 4). The interest in graft copolymers arises in part from the protection exerted by the grafts on the backbone, and this specific feature has led to a number of applications[2] as emulsifiers, surface-modifying agents, coating materials and compatibilizers in polymer blends. Amphiphilic graft copolymers, in which the solubility behavior of grafts and backbone are quite different, play an important role as emulsifiers.

The term graft copolymer should be reserved for species involving polymeric grafts; grafting of micromolecular compounds onto a polymer chain should be considered as a chemical modification of that polymer and is therefore not considered in this chapter.

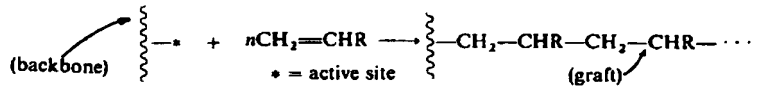
Graft copolymers in which grafts and backbone are of the same chemical nature are generally referred to as branched or comb-like polymers, in reference to their branched structure (see Volume 3, Chapter 3).[3] They evidently do not exhibit the characteristic behavior of species involving blocks of

different chemical nature. However, the methods of graft copolymer synthesis are generally applicable to comb-like polymers.

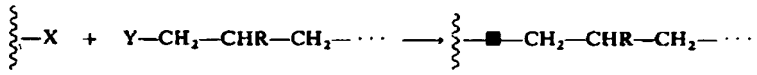
According to international nomenclature rules[4] the name of the backbone polymer should be given first, and the name of the grafts second, the word graft indicating the structure of the molecules. Thus poly(styrene-*graft*-isoprene) means that a polystyrene backbone carries polyisoprene grafts; poly[styrene-*graft*-(styrene-*co*-isoprene)] indicates that the grafts are themselves a random copolymer of styrene and isoprene. These nomenclature rules are not always obeyed and it is sometimes difficult to understand which polymer is the backbone chain and which constitutes the grafts. A term commonly used in graft copolymer formation is grafting degree, which is defined as the fraction of monomer units of the backbone which carry a graft.

12.2 PRINCIPLES OF GRAFT COPOLYMER SYNTHESIS

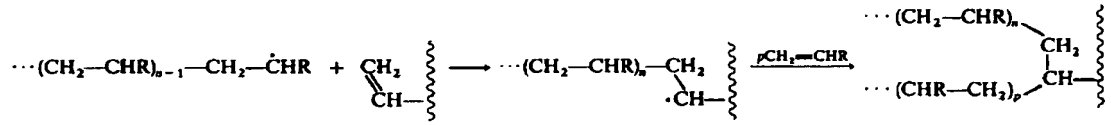
Most of the methods used to synthesize graft copolymers can be classified into three main categories (Scheme 1).[5]



Grafting from: a polymer chain carries active sites which are used to initiate the polymerization of a second monomer M



Grafting onto: a polymer chain (backbone) carrying randomly distributed reactive functions X, is reacted with another molecule carrying antagonist functions Y located selectively at its chain ends



Grafting through: a growing polymer chain incorporates a pendant unsaturation belonging to another polymer chain or to a macromonomer

Scheme 1 Methods Used for Graft Copolymer Synthesis

12.2.1 'Grafting From' Processes

A polymer chain can have initiating sites attached to it, or functions capable of generating such sites. The polymerization of a second monomer can then be initiated from the backbone chain to yield the grafts, provided that initiation occurs by addition to the incoming monomer. This method is quite general and was used in the 1950s by pioneers of macromolecular synthesis such as Smets *et al.*[6] and Bamford *et al.*[7] The sites created on the backbone can be of free radical, anionic, cationic or Ziegler–Natta type. These methods are generally referred to as 'grafting from' processes, to stress that the backbone is made first, and that the grafts are grown from it in a second polymerization process.

Though these methods are quite efficient in a number of cases, no accurate knowledge of the molecular structure of the graft copolymer formed is provided. The number of grafts is not accessible experimentally, and their length may fluctuate very much within a sample. Moreover, the graft copolymers often contain a fair amount of both homopolymers.

12.2.2 'Grafting Onto' Processes

Grafting may also result from the reaction between a polymer molecule carrying one reactive site at a chain end, and another polymer with attached antagonist functions distributed at random along its chain. In these cases grafting does not involve a chain reaction. However, it does imply that access of the functional chain end to the grafting sites is permitted. This is not obvious, owing to the well known incompatibility between polymers of different chemical natures. Such reactions are best carried out in a common solvent for both constituents to provide homogeneity of the reaction medium.

An advantage of these methods is that they allow a structural characterization of the graft copolymers formed, as backbone chain and grafts are made separately and can be characterized individually. Knowing the molecular weight of each of them, and the overall composition of the graft copolymer, it is possible to evaluate the number of grafts per chain, and the average distance between two successive grafts along the backbone. However, the absence of ungrafted homopolymer should be checked for.

These 'grafting onto' reactions have gained interest as the ionic 'living' polymerization methods[8,9] have become commonplace, giving access to polymers fitted with reactive sites at the chain ends. Their domain of application now extends far beyond these cases.

12.2.3 'Grafting Through' Processes

If the polymerization of a monomer is performed in the presence of a polymer carrying pendant unsaturations which can participate in the process, then grafting results. However, such reactions can involve formation of links between individual molecules, if a growing site happens to incorporate unsaturations belonging to two (or more) different backbones. Consequently, the process may result in crosslinked material. Measures have to be taken to avoid gel formation if soluble species are required. In any case, these methods cannot be considered as ways of access to tailor-made graft copolymers.

Another type of 'grafting through' process has attracted much interest in recent years. It involves, in a first step, the synthesis of a polymer species with a terminal polymerizable unsaturation, and referred to as a macromonomer (or macromer). Copolymerization of these species with a suitable comonomer allows easy access to graft copolymers. Each macromonomer molecule incorporated forms a unit carrying a graft.[10,11] As the macromonomer is made separately, it can be characterized independently. The backbone chain is formed upon copolymerization of the macromonomer with a suitable comonomer, using free radical initiation, and a random distribution of the grafts can be anticipated. An alternative way is to synthesize a polymer having two functions (such as –OH or $-CO_2H$) at one chain end and to build the backbone chain by a step growth (polycondensation) reaction with appropriate bifunctional compounds.[12]

12.2.4 Other Grafting Processes

Besides the three chief grafting processes described above, a number of ways of synthesizing graft copolymers have been developed which are not easy to classify unambiguously.

Grafting can result from γ- (or X-ray) irradiation of a polymer chain in the presence of a monomer.[13] The radical sites formed on the backbone can initiate the growth of the grafts and the process can be considered as a 'grafting from' reaction, although some doubts have been expressed.

Transfer reactions have also been used for grafting purposes.[14a] Some polymers exhibit rather high transfer constants, especially with respect to unstabilized radicals. If the polymerization of a monomer is carried out in the presence of such a polymer, radical sites are formed on the backbone. They can either initiate the polymerization of the monomer to build a graft, or recombine with an incoming polymeric radical. The former case is a 'grafting from' reaction, the latter 'grafting onto'. In either case homopolymer is formed simultaneously, and no real control of the process is possible.

Another interesting case of grafting involving transfer to polymer has been described by Scanlan and Merrett.[14b] On polymerizing styrene in the presence of rubber, with benzoyl peroxide (BPO) as initiator, grafting takes place. If azobis(isobutyronitrile) is used instead of BPO, no grafting is observed. This suggests that highly reactive primary radicals are responsible for attack on the rubber backbone. Free radical 'grafting from' can then occur to form the grafts. If the primary radicals are not reactive enough, polymerization takes place but no graft copolymer is formed.

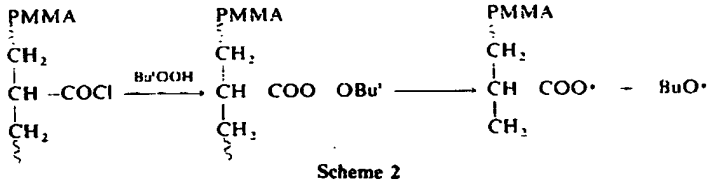
The methods used for the synthesis of block copolymers rest on the same basic principles. The only difference is the location of the sites (or reactive functions). If they are distributed at random along the backbone, a graft copolymer will result, while if they are always located selectively at chain ends, then block copolymers are formed.

The chief methods yielding well defined graft copolymers will now be reviewed and their advantages and drawbacks will be discussed.

12.3 METHODS INVOLVING FREE RADICAL POLYMERIZATION

12.3.1 Two-step Grafting Methods

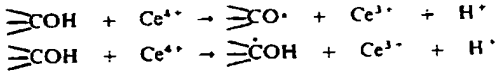
An early attempt to synthesize graft copolymers was performed by Smets *et al.*[6,15] A poly(methyl methacrylate) containing a few randomly distributed acryloyl chloride units is reacted with *t*-butyl hydroperoxide to form perester functions. Subsequently the polymer solution is heated in the presence of a second monomer, the polymerization of which is initiated by the thermal cleavage of the perester functions. The process yields both grafts (from the $-CO_2^{\bullet}$ radicals located on the backbone) and homopolymer (from the RO• radicals). Adequate fractionation is necessary to remove the latter constituent if pure graft copolymer is needed (Scheme 2).



Scheme 2

Two other free radical grafting techniques are commonly used, both based on redox radical generation (see also Volume 3, Chapter 9).

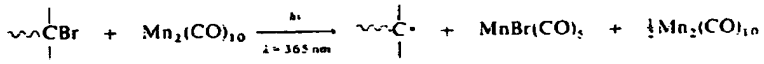
The first, introduced in the 1950s[16] and studied in great detail by Odian *et al.*,[17] applies to polymers fitted with alcohol functions, such as poly(vinyl alcohol), or poly(hydroxyethyl methacrylate), and also starch, dextranes and cellulose. It is based upon the reduction, in acidic medium, of Ce^{4+} ions by means of the alcohol functions. This reaction can be written in two ways (Scheme 3).



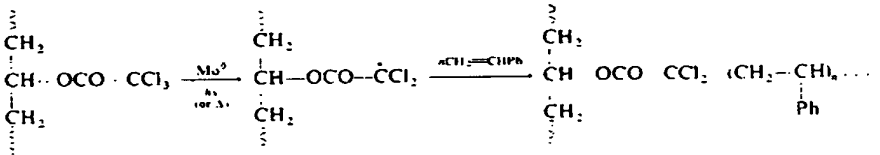
Scheme 3

If a suitable monomer is present, grafts are grown from these initiating sites. This method has been applied by Kukani and Mehta[18] to grafting polyacrylonitrile onto cellulose and by Iwakura and Imai[19] to the preparation of poly(vinyl alcohol-*graft*-methyl methacrylate). More recently, Parker *et al.*[20] have synthesized poly(vinyl alcohol-*graft*-vinylpyridine hydrochloride) and McCormick and Lin[21] have grafted polyacrylamide chains onto starch.

The other free radical grafting technique is due to Bamford *et al.*[22,23] It is based on a redox reaction between a reactive organic halide and a derivative (*e.g.* a carbonyl) of a metal in its zero oxidation state (see also Volume 3, Chapter 9). This method has been used for the synthesis of block copolymers using a terminally functionalized polymer (Scheme 4). It has been more extensively used for the synthesis of graft copolymers using, for example, poly(vinyl trichloroacetate) or functionalized polycarbonates or copolymers of them. On photoinitiation (using dimanganese decacarbonyl) or thermal initiation (using molybdenum carbonyl), grafts of poly(methyl methacrylate), polystyrene and other polymers have been grown from the backbones (Scheme 5). A potential drawback is that if the propagating grafts terminate by radical combination then networks will form at high extents of reaction. However, if polycarbonate is used as the backbone it may be degraded after grafting to allow the molecular weights and molecular weight distributions of the grafts to be determined and the kinetics of graft polymerization to be investigated.[24]



Scheme 4



Scheme 5

12.3.2 Grafting *via* Irradiation Techniques

γ-Irradiation has been used extensively to create free radical sites on polymer chains. These radicals can either initiate the polymerization of a second monomer or recombine with growing radicals, yielding the expected grafts in either case (Scheme 6). The irradiation is sometimes carried out in the absence of oxygen, to prevent peroxidation of the backbone chain. Alternately, advantage can be taken of peroxy radicals formed on irradiation of the polymer in the presence of oxygen. Several specific procedures have been developed, especially by Chapiro,[13,25] and are now in common use.

Scheme 6

(1) The 'direct radiation grafting' procedure involves swelling the polymer with another monomer followed by γ-irradiation. As radicals are formed on the polymer, they initiate the polymerization of the monomer. Grafts are grown from these sites, but homopolymer is formed simultaneously. High grafting yields and low homopolymer contents are obtained if the backbone polymer is much more sensitive towards irradiation than the monomer to be grafted, and/or if the concentration of the latter is small (in other words, low swelling degrees of the polymer are advantageous).

This method has been applied to grafting polystyrene or polybutadiene onto either a poly(methacrylic ester) or a poly(vinyl chloride) backbone. It has also been used to modify polyamide (nylon) fibers or fabrics with poly(vinylidene chloride) grafts[26] (to decrease their flammability). Permselective membranes have been made by grafting hydrophilic chains [such as poly(*N*-vinylpyrrolidone), poly(acrylic acid), or poly(vinylpyridine)] onto poly(tetrafluoroethylene) (PTFE) backbones.[25] In order to minimize the amount of homopolymer formed, inhibitors (Fe^{2+} or Cu^{2+}) are often added to the swelling medium.[27] A small amount of solvent enhances the permeation of the monomer into the polymer film. Membranes of PTFE with grafts of both poly(acrylic acid) and poly(vinylpyridine) have been obtained in two successive operations of this kind.[25] In another recent example given by Hsiue,[28] poly(vinylpyridine) has been grafted onto films of a polystyrene/polybutadiene block copolymer, yielding charged mosaic membranes.

(2) The 'preirradiation technique' also applies to bulk polymers. Trapped radical sites arise from γ-irradiation of a polymer at temperatures below its glass transition. Subsequently, the polymer is immersed in the monomer to be grafted. As the latter diffuses into the preirradiated polymer, the radicals that have been trapped initiate its polymerization. When all the sites have been consumed, the grafting process stops. The grafting degree is generally low, and it is not constant throughout the sample. It is largest at the surface, or close to it. Homopolymer is formed in low amounts only. This method is most commonly applied to thin films.[29] Isotactic polypropylene, once irradiated under vacuum, initiates the polymerization of butadiene to yield grafts. Annealing of the polypropylene film has been shown to improve the grafting yield.[29] The polymer structure is too rigid for coupling reactions to take place between macroradicals (no crosslinking is observed) but access of the monomer to the sites is improved. Kabanov *et al.*[30] have developed a similar method to graft poly(methyl methacrylate) onto cellophane. Accurate characterization of the grafts is made possible in this case after hydrolysis of the cellophane backbone.

(3) The 'peroxidation method' has also been widely used for grafting purposes. The two irradiation techniques above imply the absence of oxygen, to prevent formation of peroxy radicals which may induce chain scissions. However, irradiation of a bulk polymer can also be carried out in the presence of oxygen to obtain fairly stable peroxide sites, which may be stored for rather long times. In a second step the polymer is immersed into a monomer and heated. The peroxy radicals are themselves responsible for the formation of polymeric grafts.[31]

This method has been applied to the synthesis of charged mosaic membranes.[32] A PTFE film is irradiated in air through a brass shield to get peroxide sites over well defined geometrical portions of it. It is then immersed into acrylic acid to form the grafts. After neutralization of the acid functions, the film is once again irradiated through another brass shield to form peroxide sites in previously unirradiated parts. It is then immersed in vinylpyridine and new grafts are created. The film is thus fitted with ionogenic grafts of two different kinds located in different areas and it exhibits specific properties.

Another example has been presented by Hsuie.[33] Polyethylene films irradiated in the presence of air and stored for a couple of hours have been immersed into an aqueous solution of acrylic or methacrylic acid containing some Fe^{2+} salt. In this case, the grafting process is initiated by the redox reaction between the peroxide functions and the iron salt. The grafting ratio first increases with time and then reaches a plateau when the peroxide sites have been consumed. It is an increasing function of the irradiation dose and of the monomer concentration.

The same kind of technique has been applied by Plate[34] to the synthesis of poly(ethylene-*graft*-acrylamide), yielding similar results.

(4) γ-Irradiation of a solution containing both a polymer and a monomer has also been attempted. These systems are quite difficult to study however, since the radiolysis of the solvent may yield a large number of radicals, which will induce the formation of homopolymer. Only in the case of highly radioresistent solvents can one expect to get predominantly the 'grafting from' reaction, together with homopolymer.

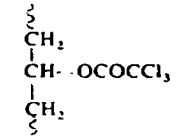
12.3.3 Grafting *via* Transfer Reactions

'Grafting onto' reactions in free radical polymerizations cannot be considered as such, since radical recombination leading to grafting is only one of many possible reactions in polymerizations involving transfer to polymer.

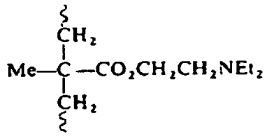
The transfer constant to one given repeat unit of a polymer is in most cases quite low, and in spite of the high number of repeat units in a polymer chain, the transfer constants to polymer are also negligible in most cases. However, there are polymers which can behave as transfer agents, especially towards unstabilized, highly reactive radical sites.

Kahrs and Zimmermann[14] have shown that if vinyl acetate is polymerized in the presence of poly(ethylene oxide) a graft copolymer results. Other examples have been given since then. Whether the radicals formed by transfer to the backbone initiate the polymerization of the monomer or recombine with growing macroradicals is not clearly established.

Quite different is the case of induced transfer to the polymer.[35] Functions that are known to exhibit high transfer constants (such as trichloromethyl or diethylaminoethyl), introduced by chemical modification or by copolymerization, are distributed at random along the backbone (Scheme 7). The polymerization of a monomer carried out in the presence of such polymer species involves a large number of transfer steps whereby grafts are formed, together with a small amount of homopolymer. The advantage is that crosslinking reactions are not expected to occur and have never been observed.



poly(vinyl trichloroacetate)



poly(diethylaminoethyl methacrylate)

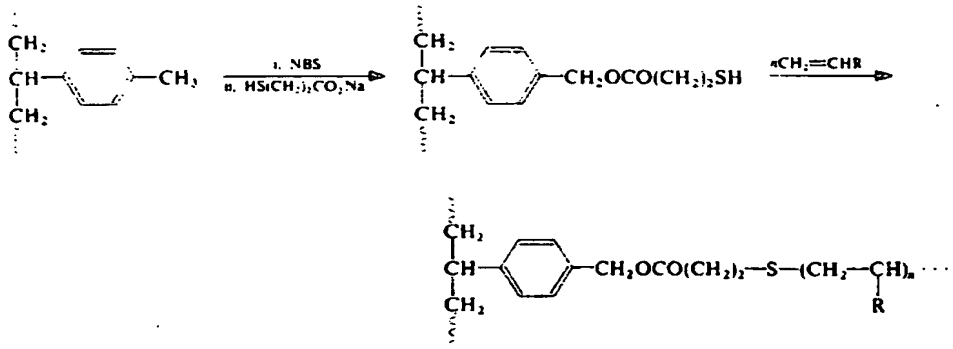
Scheme 7

An example of grafting by transfer has been disclosed recently by Piirma.[36] A poly(*p*-methylstyrene) backbone is treated with *N*-bromosuccinimide (NBS) to brominate some of the methyl groups. It is then reacted with sodium β-mercaptopropionate to give thiol functions distributed at random along the chain. Upon polymerization of *N*-vinylpyrrolidone in the presence of this polymeric chain transfer agent, graft copolymers exhibiting high grafting degrees have been obtained (Scheme 8).

12.4 ANIONIC GRAFTING PROCESSES

12.4.1 Grafting *via* Carbanionic Initiation

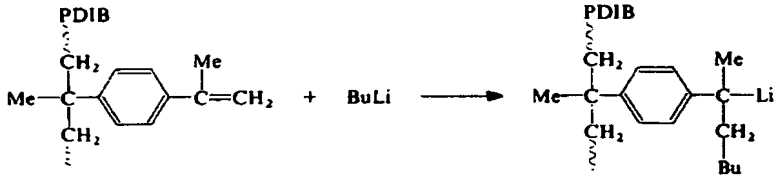
A polymeric backbone with attached organometallic sites is used as a multifunctional initiator for the polymerization of a suitable monomer to build the grafts. The chief problem here is to find satisfactory ways to obtain a macromolecule with carbanionic sites distributed at random. The



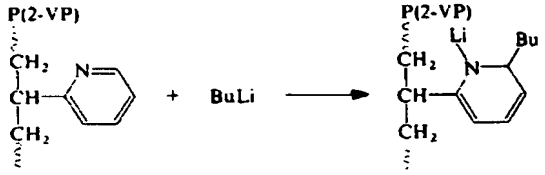
Scheme 8

metallation of a polymer can originate from addition reactions, from substitution of labile hydrogens, or from metal–halogen exchange reactions.

(1) Addition can be envisioned in a small number of cases only. Under well defined conditions, *p*-diisopropenylbenzene can be polymerized anionically to a linear polymer,[37] each unit of which bears an unsaturated side group. If these functions are reacted in benzene solution with BuLi at a temperature chosen such as to avoid propagation (*i.e.* above the 'ceiling' temperature of α-methylstyrene type units), addition of BuLi onto the unsaturations can be carried out in high yields (Scheme 9). This metallated backbone can be used subsequently as the (multifunctional) initiator for the polymerization of another monomer. Physical gelation is observed as a result of associations between organometallic sites but vanishes on deactivation. The molecular weights observed for the graft copolymers are usually higher than expected, demonstrating that some coupling may have occurred during the reaction of BuLi with the backbone. BuLi also adds onto poly(vinylpyridine) but the amidic anion has low efficiency (Scheme 10).[38]

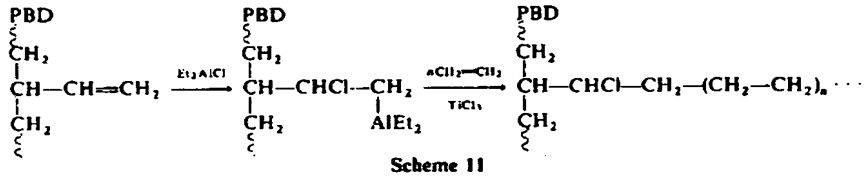


Scheme 9



Scheme 10

The addition of diethylaluminum chloride onto the pendant unsaturations of 1,2-units in polybutadiene has been studied by Greber and others.[39–41] The aluminated polymer can be reacted with ethylene in the presence of a transition metal compound ($TiCl_3$), to yield polyethylene grafts (Scheme 11). A similar method has been used to grow polyacetylene grafts from a polybutadiene

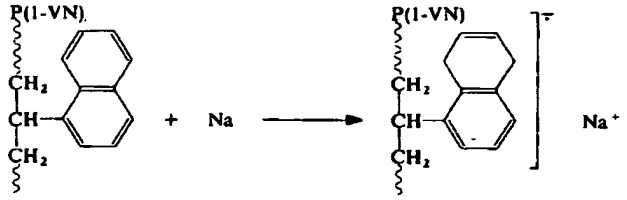


Scheme 11

backbone treated with Et_2AlCl.[42] Such methods can be considered as involving site transformation, because the growth of the grafts occurs by a Ziegler–Natta type polymerization.

(2) Electron transfer processes from an alkali metal to poly(vinylnaphthalene)[43,44] is another kind of addition reaction. It is easy to perform in THF solution, and yields radical ion sites distributed at random along the chain (Scheme 12). However, initiation of anionic polymerizations by radical ion species proceeds by electron transfer to the incoming monomer.[45] As a consequence this pathway cannot be used for the purpose of grafting, with the single exception of oxirane.[43] The same is true of polymeric radical anions obtained upon metalation of poly(vinylbenzophenone) with alkali metals.[44,46]

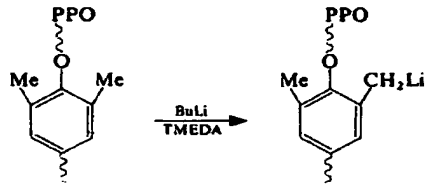
(3) Metal–halogen exchange reactions have also been applied to metalate polymeric backbones. A typical example is the reaction of potassium naphthenide onto poly(*p*-chlorostyrene) or copoly-



Scheme 12

mers thereof, at low temperature, yielding poly(*p*-potassiostyrene)[40,47,48] with almost no coupling or chain scission. A similar procedure has been applied by Popov[49] to metalate previously brominated poly(α-methylstyrene).

(4) Metalation by replacement of labile hydrogens on a polymer chain has been studied extensively. BuLi is widely used,[50–52] either alone or as a complex with tetramethylethylenediamine (TMEDA), to metalate polydienes, polystyrene (PS) or poly(phenylene oxide) (PPO) (Scheme 13). Lithiated sites are created on the aromatic nuclei as well as on methyne or methyl groups.



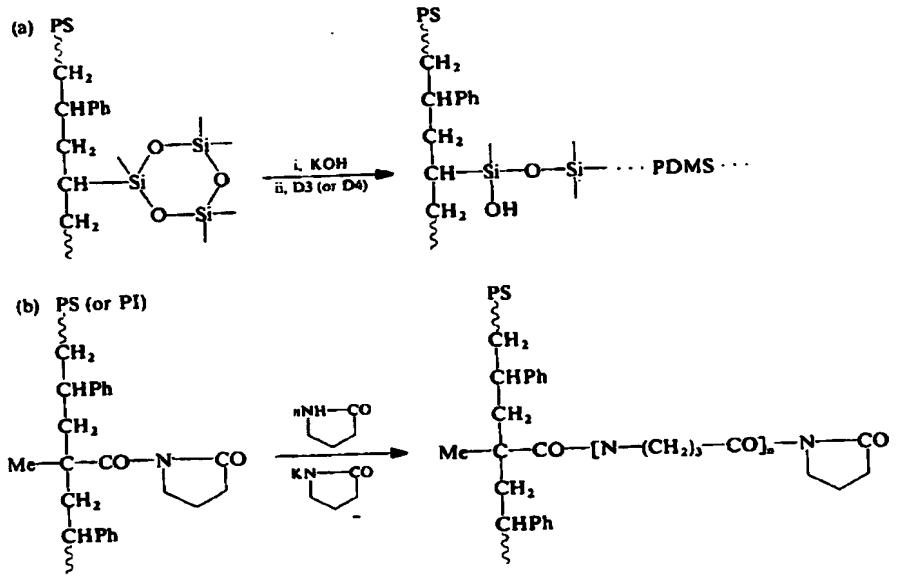
Scheme 13

The metalated sites created by any of the methods quoted are used subsequently to grow grafts from the backbone.[37–52] Although organometallic functions are often associated, even in polar solvents the general rules of anionic polymerization apply to graft-forming reactions. The nucleophilicity of the anionic sites should match the electron affinity of the monomer to get efficient initiation. Even so, it cannot be stated that all the sites have been used.

Special cases of anionic 'grafting from' reactions have been published recently. Polystyrene carrying pendant cyclosiloxane oligomeric groups are reacted with BuLi or with KOH, and the sites formed can initiate the polymerization of hexamethylcyclotrisiloxane (D3) or octamethylcyclotetrasiloxane (D4) to grow poly(dimethylsiloxane) grafts (Scheme 14a).[53] Similarly, the 'activated monomer' polymerization of a lactam can be initiated from a backbone chain carrying acyllactam functions, which are efficient promoters for the polymerization of lactams. The backbone polymer is a random copolymer of styrene and some *N*-acryloylpyrrolidone, made by free radical copolymerization. The lactam is then polymerized in the presence of the copolymer, some lactam salt being added to initiate the process. The grafting reaction reaches high yields (Scheme 14b).[54]

12.4.2 Grafting *via* Carbanionic Deactivation

Carbanionic sites are very reactive towards many electrophilic functions. This feature has been applied to the synthesis of graft copolymers, starting from backbone chains carrying electrophilic functions. To be efficient however, the grafting process requires two conditions to be fulfilled.[55]



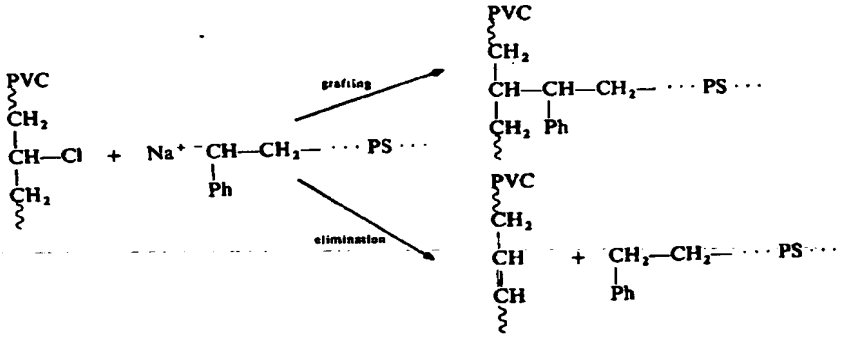
Scheme 14

(a) The nucleophilicity of the carbanion should match the electron affinity of the functions located on the backbone. This explains why most of the grafting procedures described refer to living polystyrene or polydienes involving quite reactive carbanionic sites. (b) No side reaction should be involved. The backbone should not carry any proton-donating function (acid, alcohol, amine *etc.*) which would deactivate the sites. Some elecrophilic functions also give unwanted reactions.

If the above conditions are fulfilled, grafting from reactions may lead to well defined and entirely characterizable macromolecules.[55–66] The length of the backbone and that of the grafts can be determined independently and the number of grafts can be estimated, taking into account the overall composition of the sample. It has also been shown that the distribution of the grafts is random and that within a sample the number of grafts is roughly proportional to the length of the backbone.

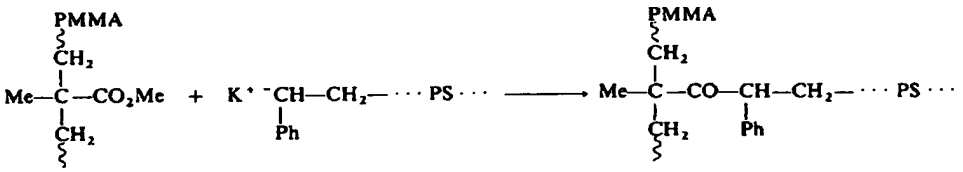
Ester, anhydride, nitrile, chlorosilane and epoxide are the electrophilic functions most commonly used for 'grafting onto' reactions with strongly nucleophilic carbanions.

With alkyl halides (*e.g.* PVC), side reactions are likely to occur. Elimination (dehydrochlorination) may compete if a strong nucleophile is used[61] (Scheme 15). Metal–halogen exchange has also been observed, especially when Li^+ is used as counterion. Benzylic and allylic halides are far more satisfactory in that respect as elimination is impossible.[58,62] Chloromethyl sites in poly(epichlorhydrin) (PEC) or in poly(dichloromethyloxetane) also react unambiguously[63] to yield graft copolymers.



Scheme 15

Many graft copolymers have been made by anionic deactivation. A typical example is the reaction of living polystyrene onto poly(methyl methacrylate).[55–57] A disadvantage of the method is that the grafts are attached to the backbone by means of carbonyl groups (Scheme 16), which are cleavable

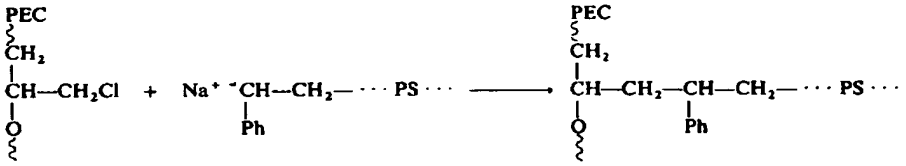


Scheme 16

photochemically. Attack of the carbonyl linkage by another living site (to yield a tertiary alcohol) is unlikely for steric reasons. However, this issue is controversial. The preparation of comb-like polymers has been performed by reaction of living polystyrene onto a polystyrene backbone carrying a known amount of randomly distributed methyl methacrylate units.[64]

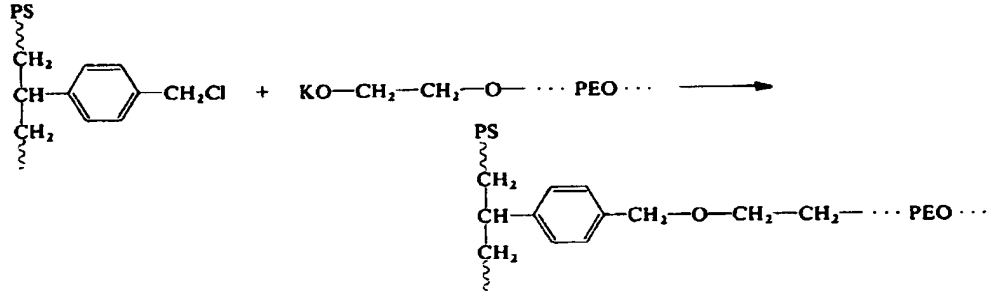
The same method has been applied by Marchessault[65] to graft polystyrene onto permethylated xylanes (the methylation being necessary to remove the proton-donating alcohol functions in the backbone).

Recently Barrie[63] has succeeded in reacting and attaching living polystyrene or similar polymers onto PEC (Scheme 17). As mentioned before, the expected reaction occurs without elimination and grafting yields are satisfactory. Reaction of living polystyrene onto poly(vinylpyridine) also yields some grafting.[38]



Scheme 17

The reaction of living poly(ethylene oxide) onto partially chloromethylated polystyrene is also quite straightforward, being an early example of the preparation of amphiphilic graft copolymers (Scheme 18).[66]



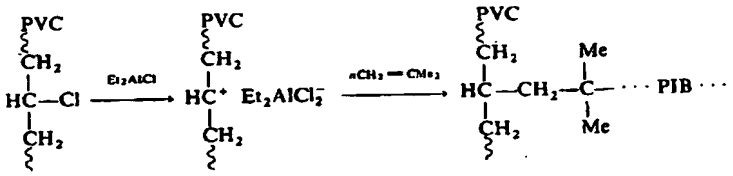
Scheme 18

12.5 METHODS INVOLVING CATIONIC POLYMERIZATION

12.5.1 Cationic 'Grafting From' Processes

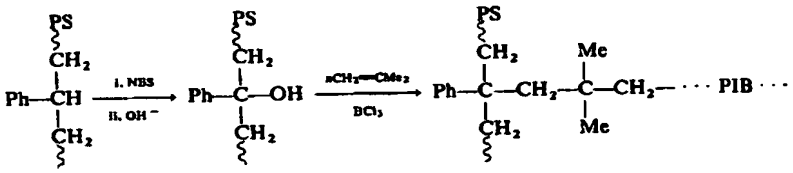
Owing to their very high reactivity, carbenium ions cannot be distributed at random along a polymer backbone and used to initiate the polymerization of a second monomer. There are only a few cases where procedures of this kind are applicable for grafting purposes: either some protection is exerted on the cationic site, to prevent side reactions, or the cationic site is formed *in situ* in the presence of the monomer for immediate use.

Cationic 'grafting from' reactions have been performed by Kennedy,[67,68] starting from backbones containing chlorine such as poly(vinyl chloride), poly(chloroprene-*co*-isoprene) and partially chlorinated styrene–butadiene rubber (SBR) and others. The grafting reaction involves monomers such as isobutene or styrene and it is generally initiated by means of diethylaluminum chloride (Scheme 19).



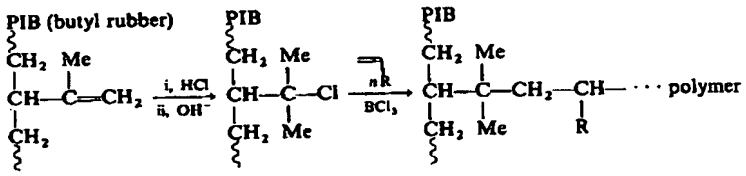
Scheme 19

A more recent example of cationic 'grafting from', also described by Kennedy, makes use of an initiating system comprising a tertiary alcohol and boron trichloride,[68–70] which has proved efficient for the polymerization of monomers such as isobutene, α-methylstyrene, indene and others. Kennedy's aim was to create tertiary alcohol sites on a polymer backbone and to react them with BCl_3 in the presence of a suitable monomer to grow the grafts. In the case of a polystyrene backbone, bromination of some tertiary carbon atoms by means of NBS is followed by alkaline hydrolysis (under conditions such as to minimize elimination reactions), to yield the tertiary alcohol functions (Scheme 20). Grafts of polyisobutene (PIB) have been grown from that backbone.



Scheme 20

Polyisobutene with some isoprene units distributed along the chain has also been used as a backbone.[69] Hydrochlorination of the double bonds followed by hydrolysis yields tertiary alcohol functions, from which polyindene grafts have been grown (Scheme 21). In both cases the graft copolymers exhibit relatively large compositional heterogeneity, which might be due to an inhomogeneous distribution of the initiating sites along the backbone.

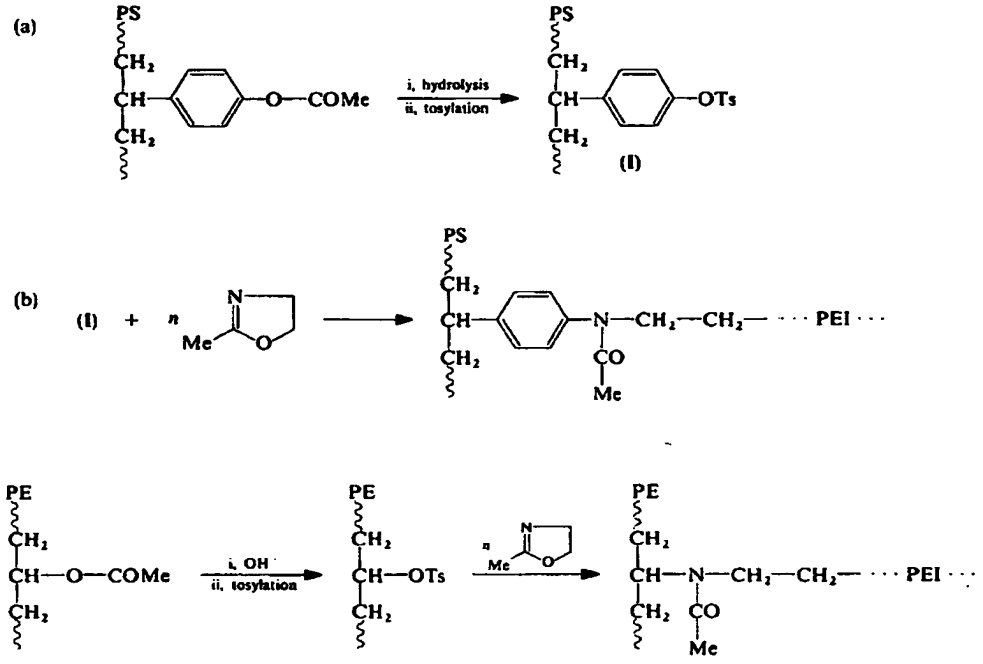


Scheme 21

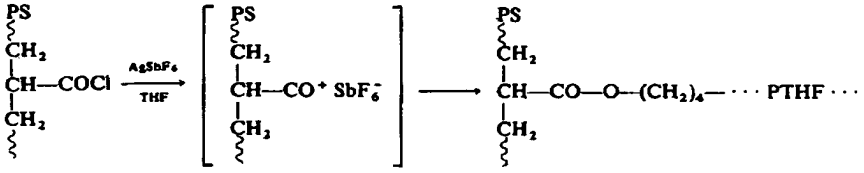
A similar method has recently been disclosed by Saegusa.[71] Poly(2-methyloxazoline) is grafted onto polymeric backbones carrying attached –OH functions. The starting point is a copolymer of styrene and *p*-acetyloxystyrene. After hydrolysis and tosylation, these sites are able to initiate the ring-opening polymerization of oxazoline (Scheme 22a). The poly(*N*-acylethyleneimine) grafts can be hydrolyzed subsequently to poly(ethyleneimine). A similar grafting process[72] involves a copolymer of ethylene and partially hydrolyzed poly(vinyl acetate) as backbone (Scheme 22b).

Cationic grafting by initiation can also be applied to other heterocyclic monomers, such as oxolane (tetrahydrofuran, THF), oxetane, or *N*-substituted aziridines. The living character of these ring-opening polymerizations is established.[73] The propagating sites are oxonium (or ammonium) salts, which are known to be far more stable than carbenium salts. In order to get satisfactory grafting efficiency, the initiating sites are made *in situ*, in the presence of the monomer.[74] Oxocarbenium salts are quite efficient initiators for these polymerizations, and this is suitable for cationic 'grafting from' reactions.[75]

The backbone chain is made by free radical copolymerization of styrene with some acryloyl chloride.[75] It is reacted in THF solution with silver hexafluoroantimonate. The oxocarbenium salt formed immediately initiates the polymerization of THF (Scheme 23). However, the growth of the grafts has to be stopped at an early stage (by induced deactivation) to prevent formation of bridges between individual chains.[76] The graft copolymers obtained have been characterized accurately.

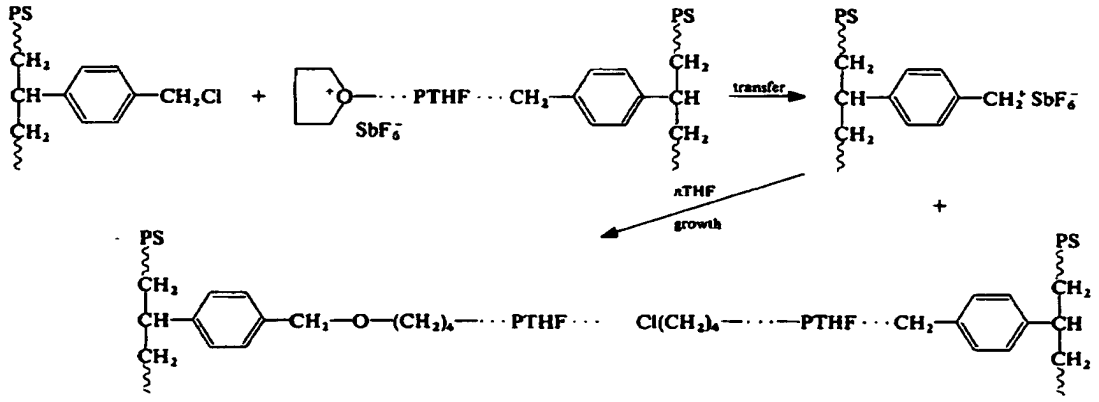


Scheme 22



Scheme 23

The same reaction has been performed with partially chloromethylated polystyrene as backbone.[76] On addition of silver hexafluoroantimonate in THF solution, the benzylic cations formed can initiate the polymerization of THF to grow the grafts. However, living poly(oxolane) reacts readily with benzylic halides, whereby the chain is terminated and another site is created (Scheme 24). In other words, transfer also contributes to the grafting process. The grafted structure



Scheme 24

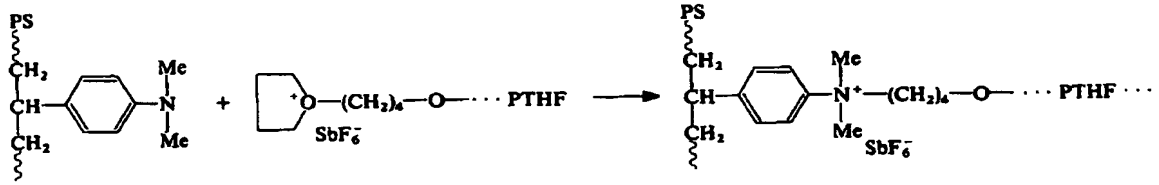
of the species obtained has been clearly established. High grafting yields can be obtained, provided the grafts are relatively short.

If the same grafting reaction is attempted with poly(vinyl chloride) (PVC) as backbone,[77] grafting occurs only onto the few allylic chlorines of the chain, which originate from the slight dehydrohalogenation that PVC always undergoes.

12.5.2 Cationic 'Grafting Onto' Processes

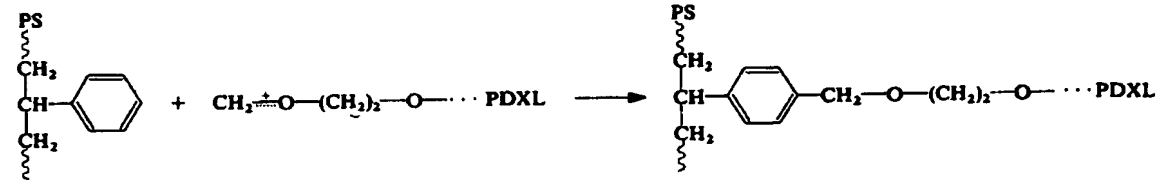
Whenever the cationic polymerization involves transfer reactions, no efficient grafting can be expected from reaction of cationic sites with nucleophilic functions distributed on a polymer backbone. However, with heterocyclic monomers the lifetime of active sites is long, and the polymers can be considered as living. Thus the opportunity is offered to carry out grafting reactions by cationic deactivation.

Successful syntheses have been carried out by Franta on living poly(THF),[78] applying the reactions of oxonium sites with nucleophilic functions that are known to give couplings. Amines are best suited for this purpose as they yield ammonium salts. Thus living polyoxolane has been reacted with poly(vinylpyridine) or with poly(*p*-dimethylaminostyrene) (Scheme 25). Graft copolymers are formed in close to quantitative amounts. The grafts are attached to the backbone by means of pyridinium (or ammonium) salt links. Goethals[79] has obtained similar results with poly-(*t*-butylaziridine).



Scheme 25

It has also been shown[80] that living polydioxolane can be reacted directly onto polystyrene, whereby grafting takes place (Scheme 26). This is a kind of Friedel–Crafts reaction, resulting from the attack of the active site onto the benzene nucleus of a monomer unit. In this case, however, polydioxolane (PDXL) may remain ungrafted. The absence of any proton-donating impurity in the medium is required. The dioxolane polymerization has to be initiated by oxocarbenium salts and not by systems containing protons.



Scheme 26

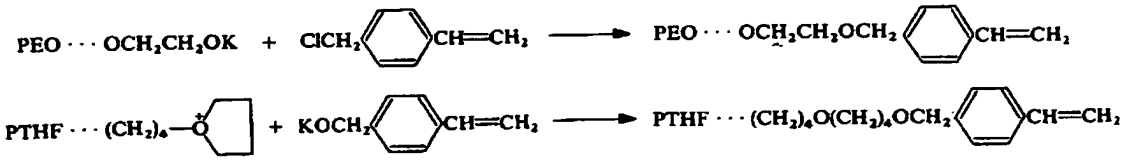
12.6 GRAFTING METHODS INVOLVING MACROMONOMERS

As mentioned earlier, macromonomers are polymers (generally of rather low molecular weight) carrying at one chain end a polymerizable unsaturation. Copolymerization of such a species with a vinylic or acrylic comonomer is a good route to graft copolymers.[10,11,81] Research on macromonomers and on their copolymerization ability has developed very rapidly over the last decade, following the pioneering work of Milkovitch.[10,82,83] The primary efforts have been aimed at finding adequate ways to synthesize macromonomers, at understanding the influence of the polymer chain they carry, and on their ability to become involved in copolymerizations.

12.6.1 Synthesis of Macromonomers

Several review articles have been devoted to macromonomer synthesis[11,81–84] (see Volume 6, Chapter 9). Obviously the ionic living polymerization methods are best suited for functionalizations at the chain ends, because they do not involve spontaneous transfer or termination reactions. However, free radical methods have also contributed substantially to the preparation of macromonomers.

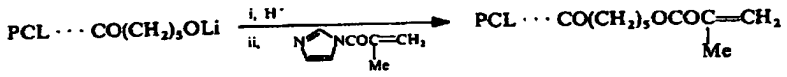
Induced deactivation of the living ionic sites is one major route to introduce the polymerizable unsaturation at chain ends. Care has to be taken, however, that no side reaction takes place simultaneously and that the active site is unable to react with the unsaturation. Typical examples include the synthesis of macromonomers—with terminal styryl or with methacrylic ester functions—upon deactivation of living anionic polymers by means of *p*-chloromethylstyrene or methacryloyl chloride (Scheme 27).[82–84,86,87]



Scheme 27

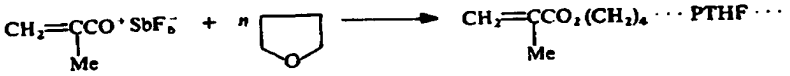
Conversely, deactivation of living cationic poly(THF) with the alkoxide derived from *p*-isopropenylbenzyl alcohol (Scheme 27)[84,86] yields an ω-styrylpolyoxolane.

Two-step procedures have sometimes been found more suitable for the synthesis of macromonomers. With poly(ethylene oxide)[88] or poly(caprolactone),[89] for instance, the living polymer has been protonated and reacted thereafter with protected esters or amines, fitted with a polymerizable unsaturation (Scheme 28). High yields can be attained, and no side reactions have been observed.



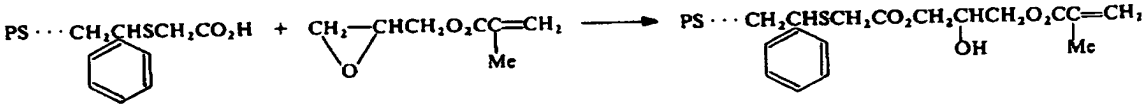
Scheme 28

Initiation of the ionic polymerization by means of an unsaturated compound may also give access to macromonomers, provided the double bond cannot get involved in the polymerization. This method chiefly applies to heterocyclic monomers such as oxolane[86,90] or oxirane,[91] the initiator being respectively methacryloyl hexafluoroantimonate or the potassium alkoxide derived from *p*-isopropenylbenzyl alcohol (Scheme 29).



Scheme 29

The synthesis of macromonomers by means of free radical techniques has been studied extensively by several authors.[85,92–94] These methods usually involve two steps. The first aims at synthesizing an ω-functional polymer. The function (in most cases $-CO_2H$ or $-OH$) is generally introduced by transfer to a functional compound exhibiting a high transfer constant, like thioglycolic acid or 2-mercaptoethanol. The second step is a classical coupling reaction involving either glycidyl methacrylate or methacryloyl chloride, to get a methacrylic unsaturation at the chain end (Scheme 30).



Scheme 30

Recently macromonomers derived from polycondensates have been prepared and studied by Percec.[95,96] Poly(phenylene oxide) and poly(ether sulfone) have been functionalized with terminal methacrylic ester unsaturations by means of phase transfer catalysis, using the functions located at the chain ends of the polycondensates.

12.6.2 Copolymerization of Macromonomers

The free radical copolymerization of a macromonomer M with a suitable comonomer A gives easy access to graft copolymers. The chief characteristic of this reaction is the large difference in molecular weights between the two species involved. Consequently, the mole fraction of macromonomer [M] in the copolymerization mixture is always low ([M] ≪ [A]). As a result, the classical equation giving the instantaneous copolymer composition

$$\frac{d[A]}{d[M]} = \frac{[A]}{[M]} \frac{r_A[A]+[M]}{r_M[M]+[A]} \tag{1}$$

reduces to

$$\frac{d[A]}{d[M]} = r_A \frac{[A]}{[M]} \tag{2}$$

It follows that the copolymerization process is in principle governed by one single parameter, the radical reactivity ratio r_A of the comonomer, a point which has been discussed in a number of recent papers.[97-102] In any case, a precise determination of the reactivity ratio of the macromonomer is difficult because of experimental inaccuracy. Another point is presently being examined thoroughly: what influence the length of the macromonomer chain has on its ability to copolymerize. This point has not yet been settled.

Many graft copolymers have been made by free radical copolymerization of ω-styryl or ω-methacryloyloxy macromonomers and various comonomers. Special interest has been devoted to amphiphilic copolymers involving a hydrophilic backbone and hydrophobic grafts, or *vice versa*.[87,94,98] Poly(perfluoroalkyl methacrylate) and poly(stearyl methacrylate) are typical examples of hydrophobic polymers, whereas poly(hydroxyethyl methacrylate) or poly(vinylpyrrolidone) are examples of nonionic hydrophilic chains. Such graft copolymers have found a number of applications as surface modifiers or coatings because of their ability to give intramolecular phase separation (surface accumulation phenomena[81]).

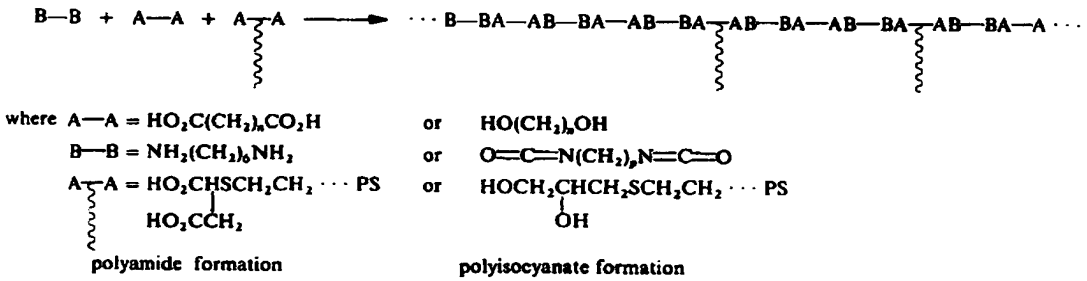
12.6.3 Polycondensation Techniques

Another kind of macromonomer has gained interest recently: polymers having two functions capable of participating in step growth polymerization reactions at one end of their chain. Such species are synthesized by free radical polymerization carried out in the presence of a bifunctional transfer agent, such as thiomalic acid or thioglycerol. Yamashita[12,103,104] has prepared a number of macromonomers of this kind, starting from various methacrylic esters.

To obtain the graft copolymer a copolycondensation involving an ω-dihydroxylic macromonomer together with a diol (such as butanediol) and a diisocyanate (toluene diisocyanate or hexamethylene diisocyanate)[103] is carried out. Alternately, an ω-dicarboxylic macromonomer is reacted with a diacid (*e.g.* sebacic acid) and a diamine (such as phenylenediamine or hexamethylenediamine) (Scheme 31).[104] The backbone chain is constructed during the polycondensation process, and each macromonomer incorporated results in a graft. This method offers interesting possibilities of grafting vinylic or acrylic chains onto a polyurethane backbone or onto a polyamide chain.

12.7 NONIONIC 'GRAFTING ONTO' PROCESSES

The last category of grafting processes to be mentioned involves reaction between two different polymers, one of which carries functions randomly distributed along the chain, the other being fitted with antagonist functions selectively located at chain ends. This type of 'grafting onto' reaction has to be compared to grafting processes involving carbanionic deactivation, already discussed (Section

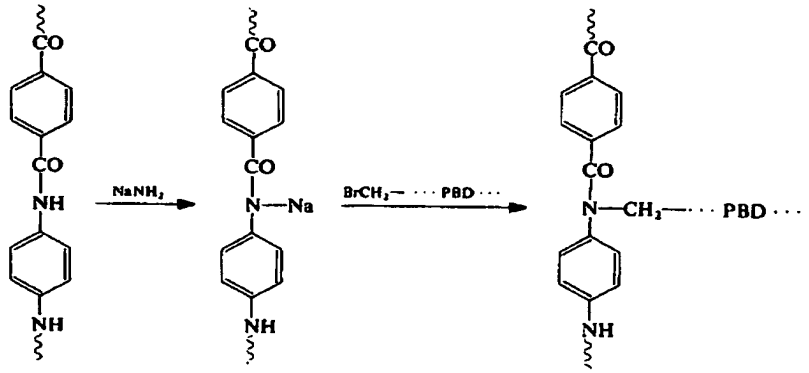


Scheme 31

12.4.2). The difference is in the nature of the chemical reaction resulting in coupling of the grafts to the backbone.

The chief difficulty arises from the incompatibility between polymers of different chemical nature. If phase separation occurs, the chance of the reaction proceeding should be greatly reduced. It is not always possible to carry out the reaction in dilute solution in order to circumvent this difficulty. Phase transfer catalysis has been found quite helpful in such instances. There are also cases where the grafting reaction proceeds in spite of the heterogeneity of the reaction medium. It should be stressed that once some graft copolymer is formed, it acts as a compatibilizer and contributes to the homogenization of the reaction mixture.

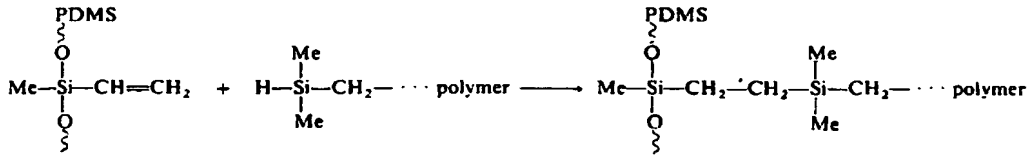
An early example of such a grafting reaction is due to Takayanagi.[105] The backbone chain of poly(*p*-phenyleneterephthalamide) is partially metalated (on the amide nitrogen) by means of sodium hydride in DMSO. The chains to be grafted are polybutadiene (PBD), with terminal brominated sites. The latter are obtained by free radical polymerization of butadiene in the presence of carbon tetrabromide. Some control of the molecular weight is provided by an adequate choice of the mole ratio of monomer to transfer agent. The coupling reaction between these two functional polymeric species yields the expected graft copolymer (Scheme 32).



Scheme 32

Phase transfer catalysis has been employed by Akashi[106] to graft polyacrylamide (with a terminal carboxylic acid function, and obtained by free radical polymerization in the presence of mercaptopropionic acid) onto a partially chloromethylated polystyrene backbone, in the presence of tetrabutylammonium hydrosulfate. The grafting yield is satisfactory.

Several examples of grafting onto reactions involving polydimethylsiloxane as the backbone are based upon the well known hydrosilylation reaction between silane functions and either vinylsilane or allylic unsaturations.[107,108] These reactions require a catalyst (generally platinum or rhodium derivatives) and are best carried out at a rather high concentration (which often implies phase separation, as mentioned above). Graft copolymers of various kinds have been obtained on reaction of polymers carrying terminal –Si–H functions with poly(dimethylsiloxane) backbones carrying a number of vinylsilane functions distributed at random (Scheme 33).[108] These backbones result from ring-opening polymerization of a mixture of octamethylcyclotetrasiloxane and its vinyl-substituted



Scheme 33

derivative. The polymer to be grafted can be made anionically, for instance by deactivation of the sites using dimethylchlorosilane.

The hydrosilylation reaction has also been employed in the reverse way.[109] A poly(dimethylsiloxane) backbone exhibiting a number of silane (Si–H) functions is reacted with a polystyrene or a poly(methyl methacrylate) fitted at its chain end with allyloxy groups. The latter species can be obtained readily by reacting a living anionic polymer first with oxirane and then with allyl bromide. The hydrosilylation reaction yields poly(dimethylsiloxane-*graft*-styrene) or poly(dimethylsiloxane-*graft*-methyl methacrylate), which have been characterized as such. They exhibit typical behavior of thermoplastic elastomers over a rather broad range of compositions.[109]

In a similar way, graft copolymers have been synthesized by reaction of a polyurethane carrying an isocyanate function at the chain end with a poly(methyl methacrylate) backbone with some pendant OH functions,[110] the latter species being obtained by free radical copolymerization of MMA with some hydroxyethyl methacrylate.

12.8 CONCLUSION

As the interest in graft copolymers has increased over the years, owing to their diversified applications in many different domains, a large variety of methods have been developed for their synthesis. Ionic living processes have contributed extensively, but they apply to a limited number of cases only. Far more general are the methods derived from free radical polymerization, which have been studied in great detail. The recent use of macromonomers for graft copolymer synthesis is also quite promising.

Some of the processes described can be termed macromolecular engineering, as they allow the possibility of accurate structure control and yield well defined species which have been characterized accurately. Such model graft copolymers are of great interest in fundamental investigations.

In other cases the graft copolymers formed are mixed with homopolymers, owing either to incomplete conversion or to side reactions. Graft copolymers often involve rather large compositional heterogeneity. However, this has no deleterious effect in most of their applications.

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